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(54) Thermostabilized copolymer composition.

(57) A stabilized composition comprising an alternating copolymer of carbon monoxide and an olefinically unsaturated compound and, based on the weight of the copolymer, from 0.03 to 5.0 %w to an additive selected from phenolic dicarboxylates, and phenolic dicarboxamides, optionally together with phenolic phosphites.

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THERMOSTABILIZED COPOLYMER COMPOSITION

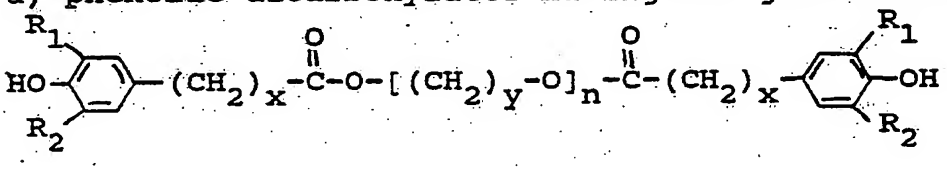
The present invention relates to copolymer compositions comprising certain additives. The relevant copolymers are characterized by having an alternating structure $[A\text{-}CO]_n$ in which A is a unit derived from an olefinically unsaturated compound. The term "copolymer" includes terpolymers in which different units A are present. As an example of suitable terpolymers reference is made to a copolymer of ethylene, carbon monoxide and propylene or butylene.

The relevant alternating copolymers and their methods of preparation are known per se, cf US-A 3 694 412, EP-A 121 965 and EP-A 181 014. Whilst these copolymers have attractive physical and mechanical properties such as yield stress, tensile strength, impact strength and flexural modulus, their processing stability and long-life or end-use stability leave room for improvement.

Applicants have found that a very large number of commercial thermostabilizers that perform well in polyamides, polyolefins, polyacrylates, polystyrenes and various other commodity thermoplastics and engineering thermoplastics fail to achieve adequate thermostabilization of alternating ethylene/carbon monoxide copolymers. It is therefore surprising to find that a few small groups of narrowly defined additives have been found that do produce the desired thermostabilizing improvement.

The present invention provides stabilized copolymer compositions comprising an alternating copolymer of carbon monoxide and an olefinically unsaturated compound and from 0.03 to 5.0 %w of an additive selected from

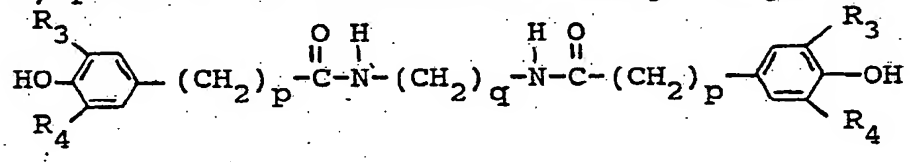
a) phenolic dicarboxylates having the general formula



(I)

in which
x is 0 to 4, preferably 2
y is 2 to 6, preferably 2 or 3
n is 2 to 8, preferably 3
R_1 is hydrogen or alkyl with 1 to 6 carbon atoms
R_2 is alkyl with 1 to 6 carbon atoms.

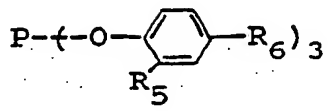
b) phenolic dicarboxamides having the general formula



(II)

in which
p is 0 to 6, preferably 2
q is 0 to 12, preferably 0 or 6
R_3 is hydrogen or alkyl with from 1 to 6 carbon atoms
R_4 is alkyl with from 1 to 6 carbon atoms, optionally together with

c) phenolic phosphites having the general formula



(III)

in which
R_5 is alkyl with from 1 to 6 carbon atoms and
R_6 is hydrogen or alkyl with from 1 to 6 carbon atoms

Suitable phenolic dicarboxylates are:
diethylene glycol bis(2-[3,5-diethyl-4-hydroxyphenyl] ethanoate); diethylene glycol bis(5-[3-isobutyl-4-hydroxyphenyl] pentanoate);
triethylene glycol bis(3-[3,5-di-tert.butyl-4-hydroxyphenyl] propanoate);
octaethylene glycol bis(2-[3,5-di-tert.amyl-4-hydroxyphenyl] ethanoate);
dipropylene glycol bis(3-[3,5-di-sec.butyl-4-hydroxyphenyl] propanoate);
tripropylene glycol bis(3-[3,5-di-tert.butyl-4-hydroxyphenyl] propanoate);
tetrapropylene glycol bis(3-sec.pentyl-4-hydroxy-benzoate);
tributylene glycol bis(3-ethyl-5-tert.butyl-4-hydroxybenzoate);
dipentylene glycol bis(2-[3-isopropyl-5-tert.amyl-4-hydroxyphenyl] ethanoate);
dihexylene glycol bis(4-[3-cyclohexyl-4-hydroxyphenyl] butanoate); and the like. Preference is given to additives in which R_2 is an alkyl group that cause steric hindrance, e.g. isopropyl, t-butyl or t-amyl. In even more preferred additives each of R_1 and R_2 is a sterically hindering alkyl group. Most preferred phenolic dicarboxylates are triethylene glycol bis(3-[3,5-di-tert.butyl-4-hydroxyphenyl] propanoate) and, tripropylene glycol bis(3-[3,5-di-tert.butyl-4-hydroxyphenyl] propanoate).

Suitable phenolic dicarboxamides are:
N,N′-bis(3-[3,5-di-tert.butyl-4-hydroxyphenyl] propanoyl) hydrazine;
N,N′-bis(2-[3-methyl-5-tert.butyl-4-hydroxyphenyl] ethanoyl) hydrazine;
N,N′-bis(3,5-isopropyl-4-hydroxybenzoyl) hydrazine; 1,1-bis(3-[3,5-di-isopropyl-4-hydroxyphenyl] propanamido) methane;
1,3-bis(4-[3-{1-methyl-cyclopentyl}-4-hydroxyphenyl] butanamido) propane;
1,5-bis(5-[3-isobutyl-4-hydroxyphenyl] pentanamido) pentane; 1,6-bis(3-sec.pentyl-4-hydroxybenzamido) hexane;
1,6-bis(3-[3,5-di-tert.butyl-4-hydroxyphenyl] propanamido) hexane;
1,8-bis(6-[3-ethyl-5-tert.butyl-4-hydroxyphenyl] hexan-amido) octane;
1,12-bis(2-[3,5-diethyl-4-hydroxyphenyl] ethanamido) dodecane; and the like. Preference is given to additives in which R_4 is an alkyl group that cause steric hindrance, e.g. isopropyl, t-butyl or t-amyl. In even more preferred additives each of R_3 and R_4 is a sterically hindering alkyl group. Most preferred phenolic dicarboxamides are N,N′-bis(3-[3,5-di-tert.butyl-4-hydroxyphenyl] propanoyl) hydrazine, and 1,6-bis(3-[3,5-di-tert.butyl-4-hydroxyphenyl] propanamido) hexane.

Suitable phenolic phosphites are:
tris(2-tert.butylphenyl) phosphite;
tris(2-tert.amylphenyl) phosphite;
tris(2,4-diethylphenyl) phosphite;
tris(2-tert.amyl-4-tert.butylphenyl) phosphite;
tris(2,4-di-isopropylphenyl) phosphite;
tris(2-isopropyl-4-tert.butylphenyl) phosphite;
tris(4-tert.butyl-2-isopropylphenyl) phosphite;
tris(2-[1-methyl-cyclopentyl] phenyl) phosphite;
tris(2-methyl-4-tert.butylphenyl) phosphite;
tris(2,4-di-tert.butylphenyl) phosphite; and the like. Preference is given to additives in which R_6 is an alkyl group that cause steric hindrance, e.g. isopropyl, t-butyl or t-amyl. In even more preferred additives each of R_5 and R_6 is a sterically hindering alkyl group. Most preferred phenolic phosphite is tris(2-tert.butylphenyl) phosphite.

When selecting a phenolic dicarboxamide in which q is 5 to 7, it is beneficial to employ such additive in admixture with a phenolic phosphite, preferably in such a mixture the phenolic dicarboxamide and phenolic phosphite are present in about equal weight proportions, i.e. 1 pbw of a phenolic dicarboxamide per 0.8 to

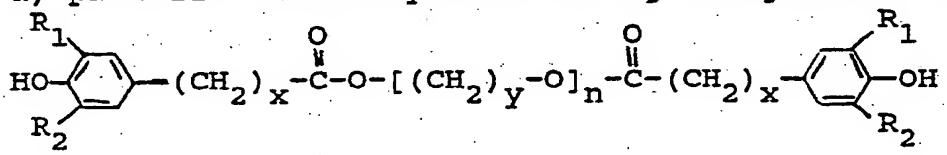
The table shows that additives 5 and 6 which are commercial top quality single thermostabilizers for polyethylenes, polypropylenes and polyamides completely fail to show an attractive performance, and since the polymer degradation mechanism of the relevant ethylene/carbon monoxide copolymers used in this invention and the physico-chemical behaviour of the additives in the copolymers are not known there is no way of predicting the favourable results obtained with the additives used in this invention.

Results at best similar to, but mostly inferior to those reported for the comparative additives in the Table hereinabove were obtained when testing many other commercial thermostabilizers for thermoplastics.

Claims

1. A stabilized composition comprising an alternating copolymer of carbon monoxide and an olefinically unsaturated compound and, based on the weight of the copolymer, from 0.03 to 5.0 %w to an additive selected from

a) phenolic dicarboxylates having the general formula



(I)

in which
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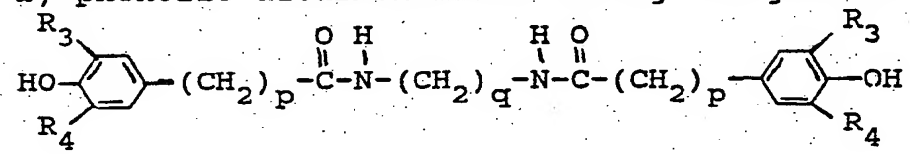
y is 2 to 6
n is 2 to 8
R_1 is hydrogen or alkyl with 1 to 6 carbon atoms
R_2 is alkyl with 1 to 6 carbon atoms.

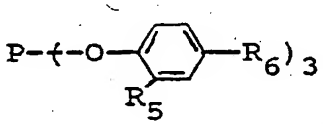
b) phenolic dicarboxamides having the general formula



(II)

in which
p is 0 to 6
q is 0 to 12
R_3 is hydrogen or alkyl with from 1 to 6 carbon atoms
R_4 is alkyl with from 1 to 6 carbon atoms, optionally together with

c) phenolic phosphites having the general formula



(III)

in which
R_5 is alkyl with from 1 to 6 carbon atoms and
R_6 is hydrogen or alkyl with from 1 to 6 carbon atoms.

2. A composition as claimed in claim 1 in which x is 2.

3. A composition as claimed in claim 1 or 2 in which y is 2 or 3.

4. A composition as claimed in any one of claims 1 to 3 in which n is 3.

5. A composition as claimed in any one of claims 1 to 4 in which p is 2.

6. A composition as claimed in any one of claims 1 to 5 in which q is 6 or 0.

7. A composition as claimed in any one of claims 1 to 6 in which R_2, R_4 and R_5 are alkyl groups causing steric hindrance.

8. A composition as claimed in any one of claims 1 to 7 in which R_1, R_3 and R_6 are alkyl groups causing steric hindrance.

9. A composition as claimed in any one of claims 1 to 8, which comprises a mixture of 1 pbw of a phenolic dicarboxamide selected from group b) and from 0.8 to 1.2 pbw of a phenolic phosphite selected from group c), q having a value of from 5 to 7.

10. A composition as claimed in any one of claims 1 to 9 in which the copolymer is a copolymer of ethylene and carbon monoxide.

11. A composition as claimed in any one of claims 1 to 9 in which the copolymer is a copolymer of ethylene, propylene and carbon monoxide.